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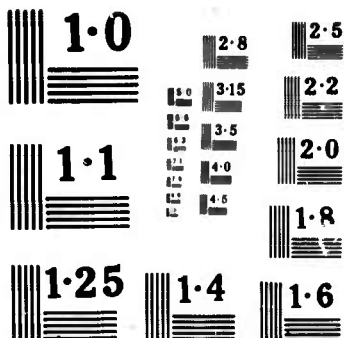
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NATIONAL BUREAU OF STANDARDS  
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# PERKIN-ELMER

THE PERKIN-ELMER CORPORATION  
(Report No. 8670)

ABSORPTION OF LIGHT IN GASES

Second Semiannual Technical Summary Report  
Through 31 December 1966

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ABSTRACT

Preliminary absorptivity data were taken with the spectrophone method and a 1.75 watt  $\text{CO}_2$  laser. Test gases included pure  $\text{CO}_2$ ; a mixture of  $\text{CO}_2$ ,  $\text{N}_2$  and He; and a sample of contaminated He. The measured absorptivity of  $\text{CO}_2$  at 10.6 microns was  $6.8 \times 10^{-4} \text{cm}^{-1}$ . This value agrees closely with the absorptivity measured by conventional spectroscopy methods. The absorptivity of the contaminated He was on the order of  $5.4 \times 10^{-5} \text{cm}^{-1}$ .

In the spectrophone method, a laser illuminates a closed sample chamber with end windows appropriate to the type of source laser. Any energy absorbed by the gas causes a temperature and pressure rise in the cell. Pressure rises as small as  $0.02 \text{ dyne cm}^{-2}$  may be observed with a pressure-measuring instrument such as a sealed capacitor microphone. In the experiment described above, the sample tube was 10 cm long. The absorption pressure signal from pure  $\text{CO}_2$  was  $630 \text{ dynes cm}^{-2}$ . However, there is a spurious long-term pressure rise of about  $1 \text{ dyne cm}^{-2} \text{sec}^{-1}$ . These results indicate that absorptivities as weak as  $10^{-8} \text{cm}^{-1}$  should be measurable when the spurious pressure rise is eliminated.

The spectrophone method with a ruby laser was used to obtain a spectrum of the water vapor absorption line at  $6943.8\text{\AA}$ . The sample was air at one atmosphere saturated with water vapor at room temperature. The peak absorptivity recorded was  $3 \times 10^{-6} \text{cm}^{-1}$ . The linewidth was less than  $0.2\text{\AA}$ .

## INTRODUCTION

The goal of this project is to measure very small absorptivities of light in gases. The method capitalizes on the high monochromatic power available from lasers. When a laser beam passes through an absorbing gas, the absorbed energy causes a temperature and pressure rise. Pressure rises as small as  $0.02\mu$  Hg can be measured without difficulty in low bandwidths. The gas absorptivity is proportional to the pressure rise. The measurement is not disturbed by a small amount of scattering in the gas.

An earlier report<sup>1</sup> described experiments to measure gas absorptivity by what is called the acoustic method. The present report describes initial experiments using the spectrophone method.

The spectrophone method is illustrated in Figure 1. The gas sample is enclosed in a cylindrical sample cell with end windows whose transmission characteristic is appropriate to the source laser. The cell radius fits the beam radius more or less closely, but not so closely that laser light incident on the tube sidewalls will cause strong desorption. A short duct connects the sample chamber to the pressure transducer. We are using the MKS Baratron, which is a sealed capacitor microphone. For a pulsed laser, the measuring bandwidth is limited by the pressure decay time constant as the heat is dissipated in the tube walls. For a CW laser, a square-wave chopping frequency may be chosen which matches the time constant for attaining the steady-state pressure. The energy or power, and the laser wavelength, are recorded along with the pressure signal.

The spectrophone method has been applied successfully with both the  $\text{CO}_2$  laser at  $10.6\mu$ , and the ruby laser. Absorptivities as weak as  $10^{-6}\text{ cm}^{-1}$  have been measured. The available sensitivity appears to be much better even than this.

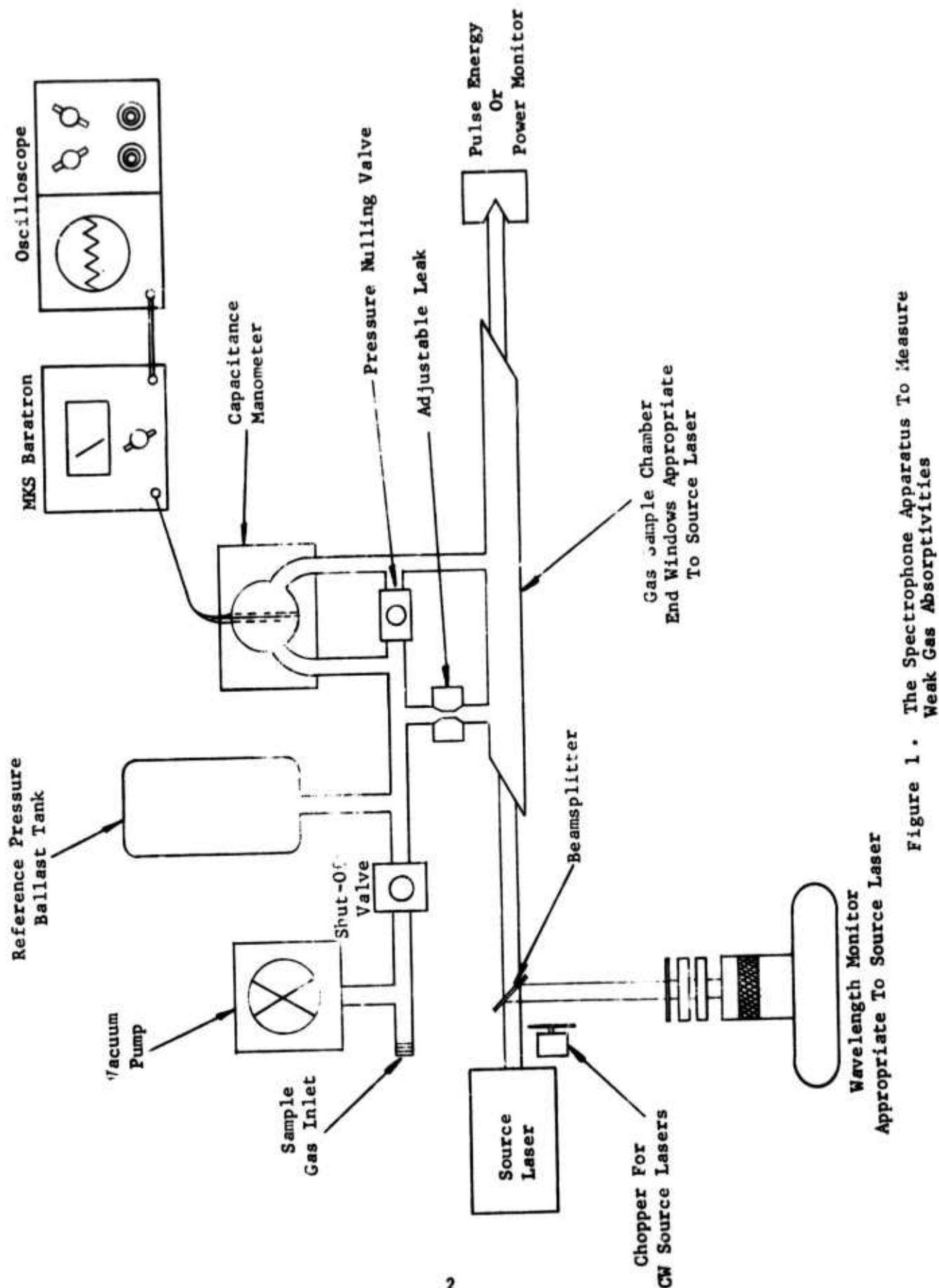


Figure 1. The Spectrophone Apparatus To Measure Weak Gas Absorptivities

EXPERIMENTS WITH THE CO<sub>2</sub> LASER AND SPECTROPHONE METHOD

Apparatus was assembled from available parts to test the feasibility of the CO<sub>2</sub> laser-excited spectrophone. The laser used was a 2-meter long, nominal 4-watt CO<sub>2</sub> laser operating at 10.6 microns. The spot size was about 1/2 cm in radius. No mode control was used. The sample cell was 10 cm long by 2 cm in radius, with NaCl end windows perpendicular to the laser beam. The cell was filled by evacuating it to 100 $\mu$  Hg, and then allowing the sample to fill it to atmospheric pressure. The pressure transducer used was the MKS Baratron, with a maximum linear range of  $\pm 1$  mm Hg. An oscilloscope and camera recorded the pressure variations about the nominal atmospheric pressure. The laser-beam chopper had a 50-percent duty cycle, and its frequency was adjustable to as low as 0.125 Hz. Power was measured with a crude water calorimeter.

EXPERIMENTAL DATA

Some of the experimental results are shown in Figure 2. The gases tested were pure CO<sub>2</sub>; laser mix, consisting of 5 percent CO<sub>2</sub>, 15 percent N<sub>2</sub>, and 80 percent He; and He with an unknown contaminant. The absorptivity of the pure CO<sub>2</sub> was so strong that the laser power input had to be reduced to 1.75 watts in order to observe the complete response within the linear range of the Baratron. This reduced power was used for all four photographs in the figure.

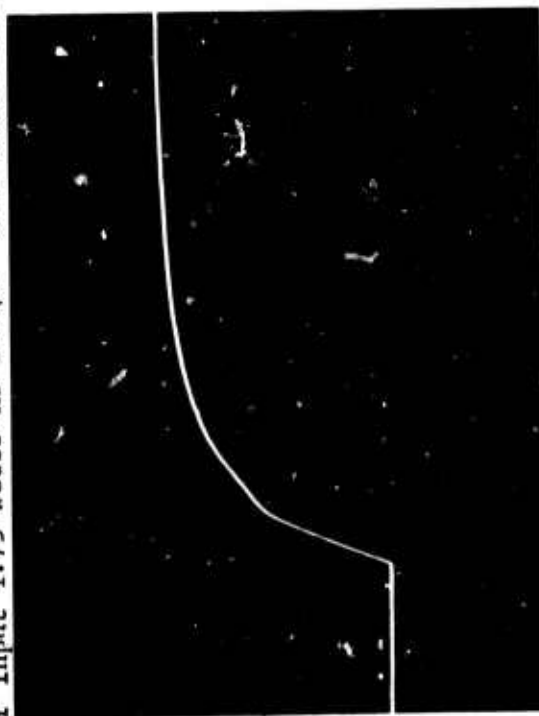
The step response of the pure CO<sub>2</sub> exhibits an interesting break point at 0.85 mm Hg pressure. The same break point is observed three times in the square-wave response, Figure 2b. We demonstrated that this break point is not of instrumental origin. It is observed when the response is started in different portions of the Baratron linear range. Also, it is not observed on the cooling cycle of the pure CO<sub>2</sub> square-wave response. The break point is due to the sudden onset of convection which tends to cool the gas more rapidly than heat conduction alone. The Rayleigh number<sup>2</sup> for CO<sub>2</sub> between parallel plates separated by 2 cm is 0.1 percent. This means a pressure



Power Input 1.75 Watts At 10.6 $\mu$ . Time Scale 2sec/cm For All Figures. Square Wave 50% Duty Cycle, 1/8 Hertz

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Report No. 8670



(a) Pure CO<sub>2</sub> Step Response



(b) Pure CO<sub>2</sub> Square Wave Response



(c) Laser Mix Square Wave Response  
5% CO<sub>2</sub>; 15% N<sub>2</sub>; 80% He



(d) Contaminated Helium Square Wave Response

differential of 0.76 mm Hg must exist between the lower and upper plates before convection can occur. A similar situation occurs in the spectrophone cell. The beam passes through the center of the cell. A temperature gradient exists between the heated gas in the beam and the cool gas near the top of the cell. Since the Rayleigh number goes inversely as the cube of the plate separation, we can eliminate this convection effect in the next apparatus by making the sample cell fit the beam more closely.

Figure 3 is a plot of the calculated step response from Appendix A. If we assume that convection is not an important source of heat loss compared with conduction, we may use Equation (A-2) to obtain the absorptivity. If  $K$  for  $\text{CO}_2$  is  $1.4 \times 10^{-4}$  watt/cm $^\circ\text{C}$ , we obtain an absorptivity  $\alpha$  of  $6.84 \times 10^{-4}$  cm $^{-1}$ . This value agrees closely with the absorptivity measured by Barker and Adel<sup>3</sup> in a 700 cm cell using conventional spectroscopy methods.

The laser mix square-wave response, Figure 2c, shows a much smaller time constant because of the high conductivity and diffusivity of helium. The response satisfies the equation

$$p = 62.5\mu \text{ Hg} [1 - \exp(-t/0.447 \text{ sec})]$$

Figure 2d shows the square-wave response of contaminated helium. The response satisfies the equation

$$p = 1.28\mu \text{ Hg} [1 - \exp(-t/0.527 \text{ sec})] + 1.07\mu \text{ Hg } t/\text{sec}.$$

The response appears to be a combination of the exponential heating response of the helium, with a short time constant, plus a heating effect with a very long time constant. In a separate experiment, this longer time constant was observed to be greater than several minutes. It is not heating and expansion of the end windows or the cell walls, as the response would then be several orders of magnitude below the observed response. We are investigating the source of this effect. Assuming the conductivity of the helium is  $14.2 \times 10^{-4}$  watt/cm $^\circ\text{C}$ , the absorptivity of the contaminant is  $5.37 \times 10^{-5}$  cm $^{-1}$ .

Pressure at  $t = 9$

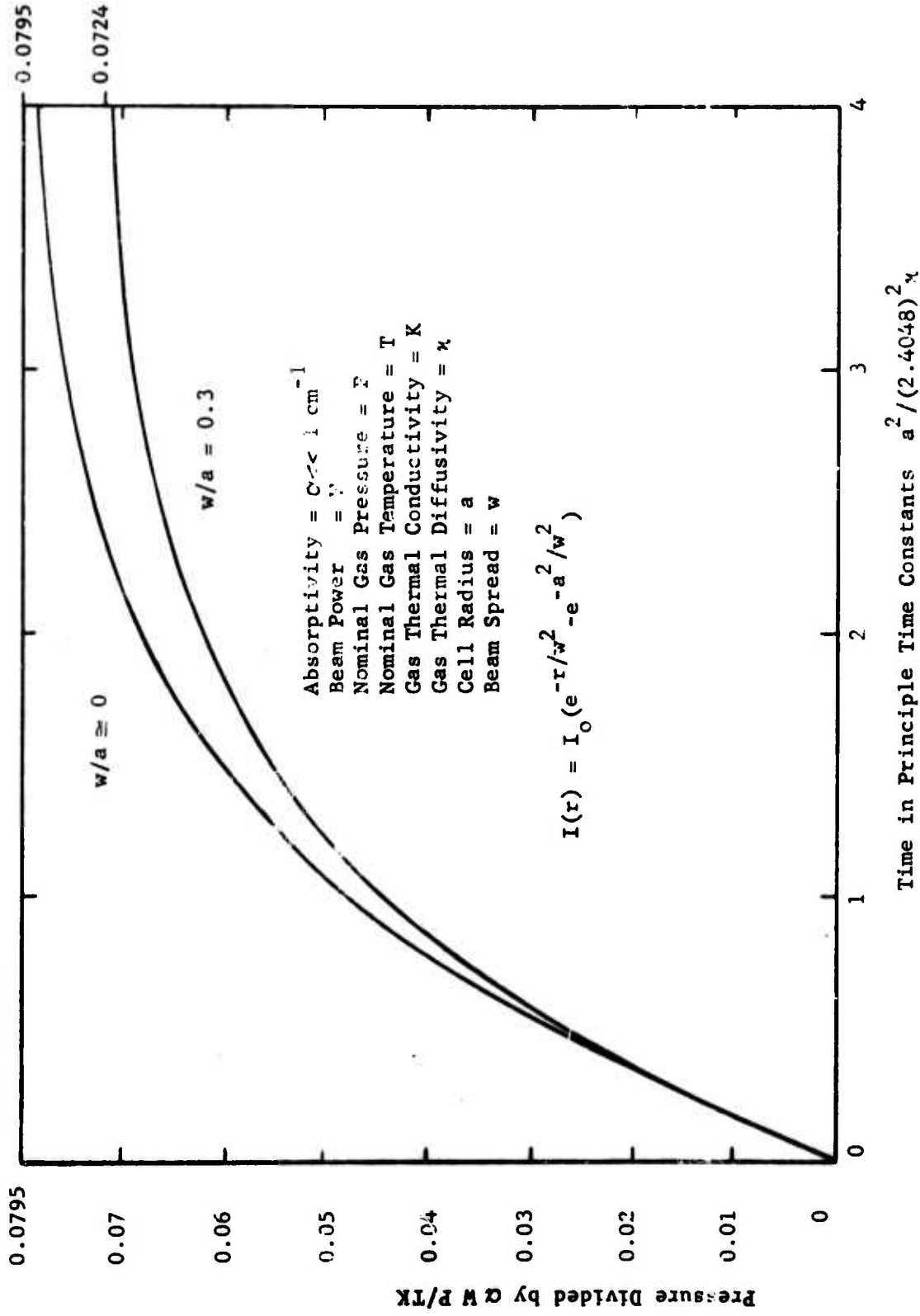


Figure 3. Absorption Cell Pressure - Step Response

SUCCESSFUL OBSERVATION OF A WEAK WATER VAPOR ABSORPTION LINE

The first absorption spectrum successfully taken via the spectrophone method is shown in Figure 4. The sample was air at one atmosphere pressure saturated with water vapor at room temperature. The absorption line shown is centered at 6943.8Å. The peak absorptivity is about  $3 \times 10^{-6} \text{ cm}^{-1}$ . This absorptivity was measured in a sample cell only 45 1/2 cm long. It represents true absorption, not absorption plus scattering. The absorption line is probably somewhat narrower than it appears in the figure. It appears to have a 0.2Å width in the figure because the ruby laser was operated with multiple modes, and because of pressure broadening. The laser pulse wavelength was scanned over a range of about 1-1/2 wave numbers by temperature tuning from 16.3°C to 37°C. (In this report, "wave number" is defined as  $1/\lambda$ .)

**EXPERIMENTAL EQUIPMENT**

The ruby laser is shown in Figure 5. (The dye cell was not present in the cavity for this experiment.) The ruby rod itself measures 1/4 inch in diameter by 3 inches in length. It is enclosed in a coolant jacket through which a mixture of methanol and water or ethylene glycol and water is circulated to maintain constant temperature and to provide temperature tuning. The helical xenon lamp may be flashed every minute and 20 seconds. Pulses of 300 to 400 millijoules may be obtained with about 10- to 15-percent repeatability without Q-switching. A calorimeter monitors the energy of every pulse. In this experiment the laser was fired by a delay system which triggered the recording oscilloscope sweep 5 milliseconds before the flashlamp. Laser pulses of 1-millisecond duration time occurred about 1 millisecond after the flashlamp was triggered.

**THE SAMPLE CHAMBER**

The sample chamber is shown in Figure 6. The laser pulse passes through the horizontal glass tube shown in the center of the tank. The tube diameter is 4-1/2mm. The laser beam is limited to a diameter of 3mm by an iris diaphragm. Careful alignment prevented the main beam from illuminating the sides of the tube. The absence of the strong pressure signal with a 1-1/2-second decay constant, which was previously observed and reported, is attributed to this

1 Atmosphere and Room Temperature

—|— Doppler Line Width at 1 Atmosphere

—|— 0.2 Å Width —|—

Typical Laser Pulse Spectrum

Absorptivity X  $10^6 \text{ cm}^{-1}$

Relative Wavenumber Scale,  $\text{cm}^{-1}$

Figure 4. H<sub>2</sub>O Vapor Absorption Line at 6943.80Å

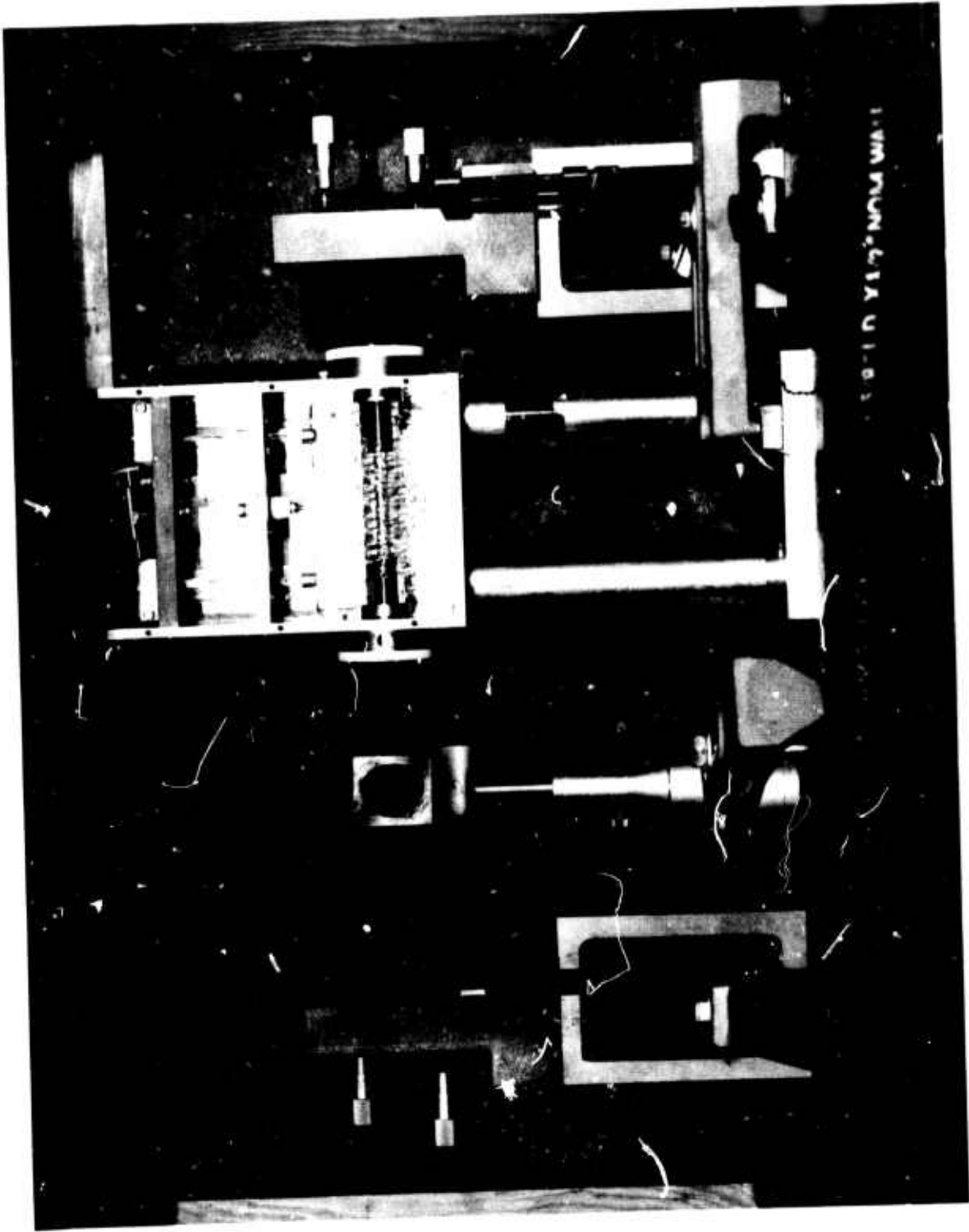


Figure 5. Temperature-Controlled Ruby Laser

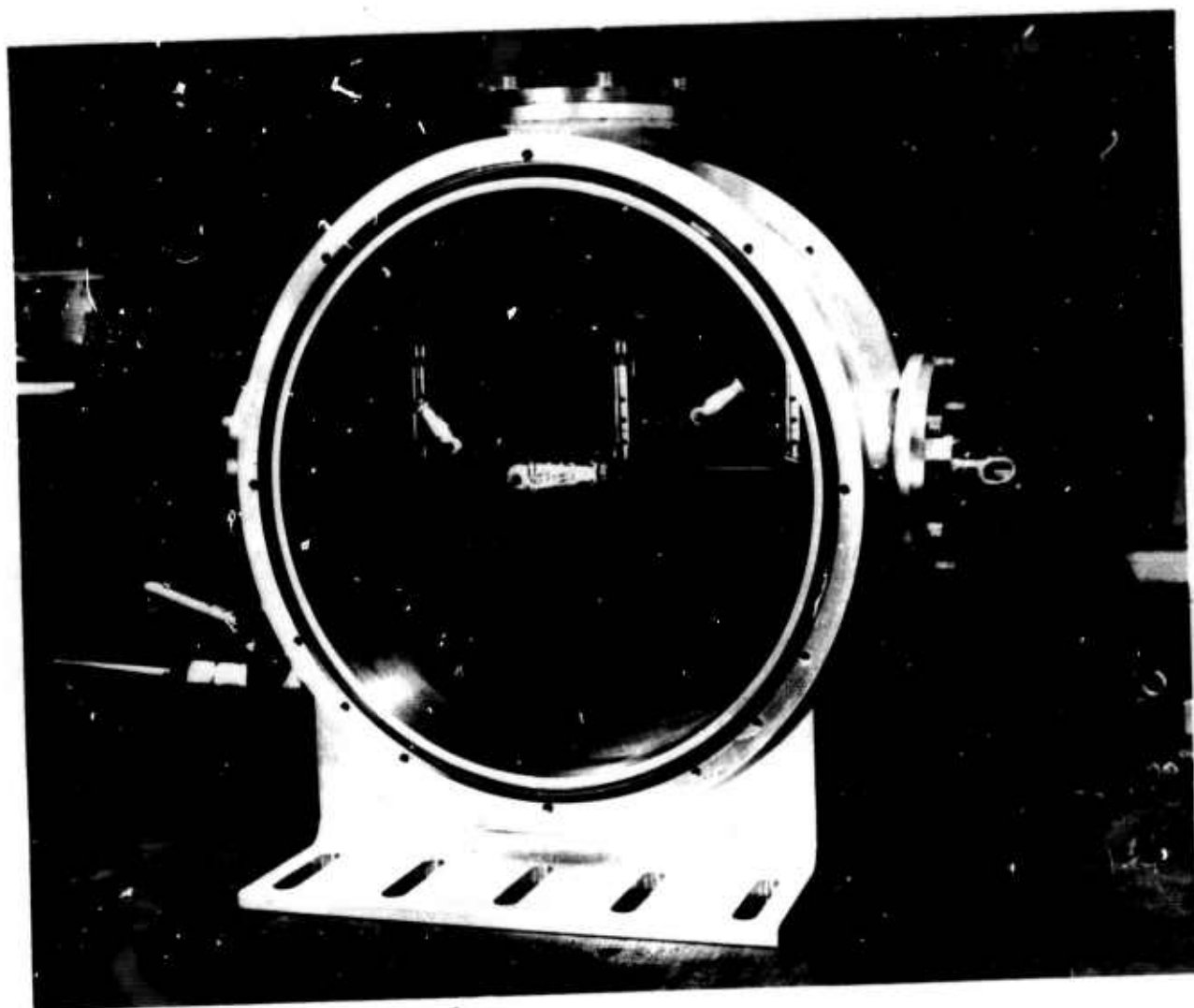


Figure 6. Gas Sample Tube in Place in Acoustic Chamber

alignment and the 3mm-diameter stop. Apparently the desorption of adsorbed gas films from the end windows of the sample chamber is less serious a problem than desorption from the chamber sidewalls.

The sample tube is housed in the acoustic pressure tank left over from experiments evaluating the acoustic method. When this tank is closed it provides approximately 30 db shielding from acoustic room noise. It also improves the thermal stability of the sample chamber.

The Baratron instrument measures the differential pressure change between the sample chamber and the surrounding acoustic tank. The instrument is attached by ducts in the back of the chamber (not shown in the figure).

Heat energy absorbed in the sample is transmitted to the sample tube walls with a time constant of 30 to 50 milliseconds. During this time the pressure difference is observed. In order to prevent a pressure buildup between the sample chamber and the surrounding acoustic chamber, the sample chamber is provided with a capillary leak. This is the glass tube projecting upwards in the figure. This leak was adjusted to have a time constant of 3 seconds (ten times longer than the pressure signal time constant). The calibration photo is shown in Figure 7.

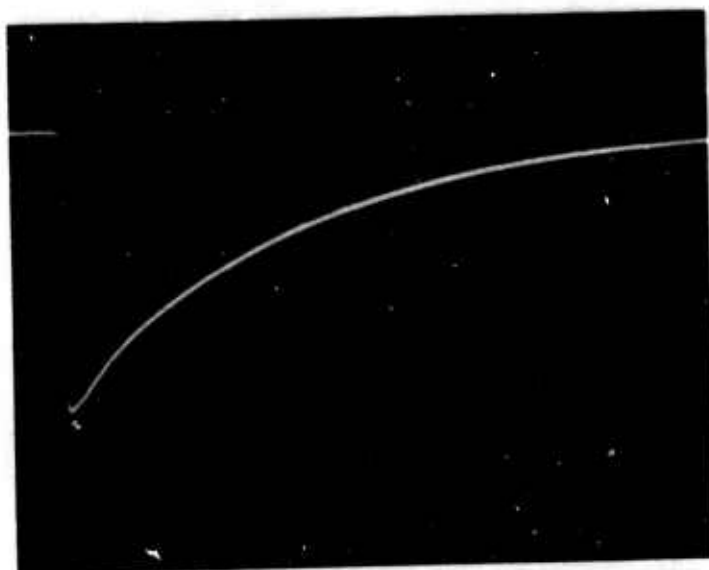
The two stopcocks on the side arms of the sample chamber permit the introduction of samples.

The end windows of the sample chamber and the windows of the acoustic chamber are set at Brewster's angle to minimize reflection loss and to improve the accuracy of calorimeter readings of the laser pulse energy.

#### EXPERIMENTAL PROCEDURE

The sample was prepared by passing air saturated with water vapor at room temperature through the sample tube for approximately 15 minutes. Then, the sample tube was closed except for the capillary leak. A few drops of water remained in the sample tube (not in the path of the beam) to insure that the air would remain saturated with water vapor. The partial water vapor pressure was approximately 17mm Hg.





Pressure Step: -10mm Hg  
Time Scale: 1 sec/cm

Figure 7. Pressure Step Response of Sample Chamber  
With Capillary Leak Open

The ruby laser was pulsed at 1-minute 20-second intervals. A calorimeter measured the pulse energy. An oscilloscope attached to the Baratron output recorded the pressure signals. The etalon and camera system recorded the laser pulse wavelength. A Fenwall temperature controller and thermistor were used to measure the ruby temperature. This temperature was recorded periodically. The coolant temperature rose on the average of 0.2 to 0.3 of a degree centigrade for each laser pulse. After 54 pulses, the temperature had risen from 16.3°C to 37°C. The change in ruby temperature caused the wavelength to scan over a 1-1/2 wave number range.

A test was made to determine any spurious effects on the signal due to acoustic noise generated by pulsing the laser. The pressure signal was recorded when the laser was pulsed but a stop prevented the laser beam from entering the sample chamber. In each test case no pressure signal was observed on the Baratron output. Therefore, the absorption measurement is not disturbed by the noise of the pulsed laser.

Timing signals were provided to start the sweep in the recording oscilloscope and then to trigger the laser pulse 5 milliseconds later. This system permitted observation of the pressure in the sample chamber just before the laser pulse and for approximately 120 milliseconds after the laser pulse. The laser pulse itself lasted for about 1 millisecond and started approximately 1 millisecond after it was triggered. Thus by the time the first 7 milliseconds elapsed, the laser pulse was over.

Typical data are shown in Figure 8. The Baratron and oscilloscope scale factors were set so that a 1-centimeter pressure signal corresponds to a 1.5 $\mu$  Hg observed pressure rise. The sweep rate was 20 milliseconds per centimeter. These photographs are reproduced in one to one ratio. The signals in the upper photograph correspond to data plotted in the left portion of Figure 4. The lower photograph corresponds to data plotted in the right portion of Figure 4. These particular data are the signals resulting from pulse numbers 6 through 10 and 41 through 45, respectively. The laser pulse energy and the laser temperature are also indicated. Note that as the temperature became greater, the pulse energy went down. The photographs from the series etalon

# PERKIN-ELMER

Laser  
Pulse  
Energy  
m joules

Pressure Pulses  
20 msec/cm x 1.5 $\mu$ Hg/cm

Ruby  
Temperature  
C

Series Etalon Photographs  
Etalon Spacing 5mm

340 10

19.2

347 9

21.0

344 8

20.5

366 7

-

346 6

19.8

266 45

-

242 44

33.8

258 43

33.3

254 42

33.0

260 41

32.9

Pulse  
No.

Pulse  
No.

Figure 8. Typical Data for the H<sub>2</sub>O Absorption Spectrum

system are side by side with the photographs of the pressure pulses, and correspond to one another as labeled. The spacing of the etalon which produced the large outer rings was 5 mm.

#### DATA REDUCTION AND CALCULATIONS

A table giving the laser pulse number, the laser pulse energy reading, the pressure signal amplitude, the wavelength shift data measured from the series etalon photographs, and the temperature was prepared. Pressure signal amplitude was measured from the base line established by the start of the pressure signal to the peak amplitude at about 1-1/2 centimeters from the start of the trace. The reading from the series etalon photographs was a measurement of the diameter of the inner pair of rings from the 5 mm etalon. When this reading was made, an average of the intensity in each separate mode was made. The diameter recorded is the diameter corresponding to the maximum intensity in the pulse. The rings from the long etalon appearing as a small spot in the center of the series etalon photographs were not used since the laser was not Q-switched and many modes were mixed.

The true pressure rise is defined as the measured pressure rise divided by a volume reduction factor. The laser pulse illuminates only a small volume of the gas contained within the sample chamber. However, the pressure rise is not measured until it is transmitted uniformly throughout the volume of the gas. The volume reduction factor is the ratio of the illuminated gas volume to the total volume of gas contained in the tube. The gas absorptivity is now calculated from the following formula:

$$\alpha = F \Delta p \pi r^2 \rho C_v T / EP$$

where  $\alpha$  is the absorption coefficient,  $\Delta p$  is the measured pressure rise,  $F$  is the volume reduction factor,  $r$  is the beam radius,  $\rho$  is the gas density,  $C_v$  is the heat capacity of the gas at constant volume,  $T$  is the absolute temperature of the gas,  $E$  is the pulse energy and  $P$  is the nominal gas pressure.

PLANS FOR THE FUTURE

The present CO<sub>2</sub> laser-excited spectrophone is somewhat limited in sensitivity by the long-term ramp response noted earlier. The source of this spurious signal must be found and reduced. Synchronous chopping and detection will be used to increase the sensitivity.

A new sample cell for the CO<sub>2</sub> laser spectrophone will be constructed. The cell will be evacuable and capable of maintaining a pressure as low as 10 $\mu$  Hg. This will make it possible to measure gas absorptivities at low pressures. If it is feasible, we will obtain some profile data on the absorption bands by scanning the wavelength of the CO<sub>2</sub> laser over one of its operating lines.

We will determine maximum sensitivity for two different cases. The first case will be sensitivity to strong absorbers at low pressures. The second case will be the measurement of the absorptivity of pure helium contaminated with known amounts of an absorbing gas.

An attempt will be made to measure the modulation of the Stark shift in ammonia or methyl-ethylamine or other molecules capable of strong Stark shift.

If time and funds permit, we will observe the band profile of water vapor under self-pressure broadening for the three absorption lines at 6942.15 $\text{\AA}$ , 6942.37 $\text{\AA}$ , and at 6943.80 $\text{\AA}$ .

## APPENDIX

THE ABSORPTION CELL PRESSURE RESPONSE  
TO A GAUSSIAN DISTRIBUTED SOURCE BEAM

The average pressure rise in the absorption cell can be calculated from the temperature distribution and the ideal gas law. In this analysis the gas absorptivity may be determined from the average pressure rise if the thermal conductivity is known. The thermal diffusivity can be found from the initial rate of pressure rise.

## COORDINATES AND GEOMETRY OF THE HEAT FLOW PROBLEM

Assume the cell is long and thin, so heat loss through the end windows is small compared with heat loss to the walls. Let the laser beam have a Gaussian intensity distribution and cylindrical symmetry. This reduces the problem to one-dimensional heat flow.

Let  $a$  = cell radius

Let  $I'(\rho)$  = beam intensity distribution

$$I'(\rho) = (W/\pi w^2) \exp(-\rho^2/w^2)$$

where  $W$  = beam power,

$w$  = beam spread (half-width at  $e^{-1}$  points).

Let  $r = \rho/a$  = dimensionless radial coordinate.

Thus the dimensionless cell radius is 1.

Let  $b = w/a$ , the fraction of the cell radius occupied by the beam.

$$\text{Thus } I'(r) = (W/\pi a^2 b^2) \exp(-r^2/b^2).$$

The intensity at the cell walls is  $(W/\pi a^2 b^2) \exp(-1/b^2)$ . It is desirable to have an intensity distribution which becomes 0 at  $r = 1$ . Hence, define a new intensity distribution.

$$I(r) = (W/\pi a^2 b^2) \left[ \exp(-r^2/b^2) - \exp(-1/b^2) \right].$$

When  $b \ll 1$ , the intensity is only slightly reduced, but the heat flow problem is made much more tractable by eliminating infinite gradients at the tube walls.

Let  $\alpha$  = gas absorptivity per unit length. Assume  $\alpha \ll 1$ , so the absorbed power per unit length is  $\alpha W$ .

Let  $A$  = rate of heat generation per unit volume per unit length in the cell. Let the unit volume be  $a^2 \cdot 1$  unit length, so

$$A(r) = (\alpha W/\pi b^2) \left[ \exp(-r^2/b^2) - \exp(-1/b^2) \right].$$

#### SEPARATION OF THE HEAT FLOW PROBLEM

Let  $\theta = \theta(r, t)$  = temperature in the cell above ambient temperature.

The heat flow equation is

$$\partial^2 \theta / \partial r^2 + r^{-1} \partial \theta / \partial r = a^2 \kappa^{-1} \partial \theta / \partial t - A(r)/K$$

where  $\kappa$  = gas thermal diffusivity =  $K/\rho C_v$

$K$  = gas thermal conductivity

$\rho$  = gas density

$C_v$  = gas specific heat capacity at constant volume

Initial condition:  $\theta(r, 0) = 0$

Boundary conditions:  $\theta(1, t) = 0$ ,  $\theta(0, t) \neq \infty$

The first boundary condition is justified because the cell walls have a much higher heat capacity than the gas. The second boundary condition is required on physical grounds.

The heat flow problem may be separated into the steady-state solution and the transient solution. Let  $\theta = u(r, t) + v(r)$ . Then  $v$  satisfies the steady-state equation

$$d^2v/dr^2 + r^{-1}dv/dr = -A(r)/K$$

subject to  $v(0) \neq \infty$ ,  $v(1) = 0$ . Also  $u$  satisfies the transient solution equation

$$\partial^2 u / \partial r^2 + r^{-1} \partial u / \partial r = a^2 \kappa^{-1} \partial u / \partial t$$

subject to  $u(0, t) \neq \infty$ ,  $u(1, t) = 0$

and  $u(r, 0) = -v(r)$ . Obviously the steady-state problem must be solved first.

#### THE STEADY-STATE TEMPERATURE DISTRIBUTION

Multiplying the steady-state equation by  $r$ , we have

$$d(r dv/dr)/dr = -(aW/K\pi b^2)r \left[ \exp(-r^2/b^2) - \exp(-1/b^2) \right].$$

Integrating and dividing by  $r$ , we obtain

$$dv/dr = (aW/K\pi) \left[ \exp(-r^2/b^2)/2r + \exp(-1/b^2)r/2b^2 \right] + C_1/r.$$

The first exponential factor can be integrated term by term. Replace it with

$$1/2r + (1/2) \sum_{n=1}^{\infty} (-1)^n r^{2n-1}/b^{2n} n!$$

and integrate to obtain

$$v = (aW/K\pi) \left[ (1/4) \sum_{n=1}^{\infty} (-1)^n (r/b)^{2n}/nn! + (1/2) \ln r + (r^2/4b^2) \exp(-1/b^2) \right] + C_1 \ln r + C_2.$$

To satisfy  $v(0) \neq \infty$ , let  $C_1 = -aW/2K\pi$



To satisfy  $v(1) = 0$ , choose  $C_2$  so

$$v = (\omega W/4\pi K) \left[ \sum_{n=1}^{\infty} (-1)^n (r^{2n}-1)/b^{2n} n! + \exp(-1/b^2) (r^2-1)/b^2 \right]$$

#### THE STEADY-STATE PRESSURE

The relation between the pressure rise and the temperature rise is found by differentiating the ideal gas law,

$dp/P = dT/T$  where  $P$  is the nominal pressure and  $T$  is the absolute ambient temperature. The average pressure  $p$  is found by the integral

$$p_1 = (2\pi \text{ 1 unit length}/V)(P/T) \int_0^1 v(r) r dr$$

where the dimensionless volume  $V = \pi l^2 \text{ 1 unit length}$ . Hence

$$\begin{aligned} p_1 &= (2P/T) \int_0^1 v(r) r dr \\ &= (\omega W P/4\pi K T) \left\{ \sum_{n=1}^{\infty} (-1)^n \left[ r^{2n+2}/(n+1) - r^2 \right] / b^{2n} n! \right. \\ &\quad \left. + \exp(-1/b^2) (r^4/2 - r^2)/b^2 \right\} \Big|_0^1 \\ &= (\omega W P/4\pi K T) \left[ \sum_{n=1}^{\infty} (-1)^{n+1} / b^{2n} (n+1)! - \exp(-1/b^2) / 2b^2 \right] \\ &= (\omega W P/4\pi K T) \left[ 1 - b^2 + \exp(-1/b^2) (b^2 - 1/2b^2) \right] \\ \text{Let } B = B(b) &= \left[ 1 - b^2 + \exp(-1/b^2) (b^2 - 1/2b^2) \right] \end{aligned}$$

Then the absorptivity is

$$\alpha = p_2 4\pi K T / W P B$$

(A-1)

Table A-1 gives values of  $B$  for cases of interest.

TABLE A-1

b	$\cong 0$	0.20	0.25	0.30
B	1	0.960	0.938	0.910

# THE TRANSIENT TEMPERATURE SOLUTION

A solution of the transient temperature solution yields the gas thermal diffusivity in terms of the amplitude and initial slope of the pressure rise.

Assume that  $u(r, t) = R(r) T(t)$ . The heat flow equation becomes

$$R^{-1} (d^2 R / dr^2 + r^{-1} d R / dr) = a^2 \kappa^{-1} T^{-1} dT / dt = -\xi^2$$

where  $-\xi^2$  is an arbitrary constant.

The solutions are

$$T = \exp(-\kappa \xi^2 t / a^2) \text{ and}$$

$$R = C J_0(\xi r) + D N_0(\xi r)$$

Since  $u(0, t) \neq \infty$ ,  $D = 0$ . To satisfy  $u(1, t) = 0$ , chose  $\xi = \xi_m$ , where

$\xi_m$  is the mth root of  $J_0(\xi) = 0$ .

The general solution so far is

$$u(r, t) = \sum_{m=1}^{\infty} C_m J_0(\xi_m r) \exp(-\kappa \xi_m^2 t / a^2)$$

To satisfy the initial condition,

$$u(r, 0) = \sum_{m=1}^{\infty} C_m J_0(\xi_m r) = -v(r),$$

multiply both sides of the equation by  $r J_0(\xi_k r)$ , integrate from 0 to 1, and use the orthogonality properties of the Bessel functions to obtain

$$\begin{aligned}
 C_k &= - \left[ 2/J_1^2(\xi_k) \right] (\alpha W/4\pi K) \cdot \\
 &\cdot \left[ \sum_{n=1}^{\infty} (-1)^n (n! n b^{2n})^{-1} \int_0^1 (r^{2n+1} - r) J_0(\xi_k r) dr \right. \\
 &\quad \left. + b^{-2} \exp(-1/b^2) \int_0^1 (r^3 - r) J_0(\xi_k r) dr \right] \\
 &= \left[ 2/J_1(\xi_k) \xi_k \right] (\alpha W/4\pi K) \cdot \\
 &\cdot \left\{ \sum_{n=1}^{\infty} (-1)^n (n! n b^{2n})^{-1} \left[ 1 - \left( \xi_k/J_1(\xi_k) \right) \int_0^1 r^{2n+1} J_0(\xi_k r) dr \right] \right. \\
 &\quad \left. + 4 \exp(-1/b^2)/b^2 \xi_k^2 \right\}
 \end{aligned}$$

#### THE TRANSIENT PRESSURE SOLUTION

The transient pressure may now be determined as before.

$$\begin{aligned}
 p_2(t) &= (2P/T) \int_0^1 u(r) r dr \\
 &= (2P/T) \sum_{m=1}^{\infty} C_m J_1(\xi_m) \xi_m^{-1} \exp(-\kappa \xi_m^2 t/a^2) \\
 &= (\alpha W P/4\pi K T) \sum_{m=1}^{\infty} D_m \exp(-\kappa \xi_m^2 t/a^2)
 \end{aligned}$$

$$\begin{aligned}
 \text{where } D_m &= (4/\xi_m^2) \left\{ 4 \exp(-1/b^2)/b^2 \xi_m^2 \right. \\
 &\quad \left. + \sum_{n=1}^{\infty} (-1)^n \left[ 1 - \left( \xi_m/J_1(\xi_m) \right) \int_0^1 r^{2n+1} J_0(\xi_m r) dr \right] / n! n b^{2n} \right\}
 \end{aligned}$$

The integral in  $D_m$  decreases with increasing  $n$  and with increasing  $m$ . It may be evaluated by successive applications of integration by parts.

We found evaluation by direct Simpson integration to be simple and precise.

Table A-2 gives the coefficients for  $m=1$  through 20, and for various values of  $b$ .

TABLE A-2

VALUES OF  $D_m$ 

m	b	0	0.20	0.25	0.30
1		-1.1080	-1.0358	-1.0123	-0.9728
2		0.1398	0.1045	0.8683	0.0704
3		-0.0455	-0.0211	-0.0141	-0.0084
4		0.0210	0.0056	0.0024	0.0009
5		-0.0116	-0.0010	-0.0004	-0.0001
6		0.0072	0.0004		
7		-0.0048			
8		0.0034			
9		-0.0025			
10		0.0019			
11		-0.0015			
12		0.0012			
13		-0.0010			
14		0.0008			
15		-0.0007			
16		0.0005			
17		-0.0005			
18		0.0004			
19		-0.0004			
20		-0.0003			

# THE TOTAL PRESSURE RISE

Let  $p$  = total pressure rise =  $p_1 + p_2(t)$ ,

$$p = (\omega P / 4 \pi K T) \left[ B(b) + \sum_{m=1}^{\infty} D_m \exp (-\kappa \xi_m^2 t / a^2) \right]$$

Let  $P(\infty) = A$ , the final amplitude of the step response.

The diffusivity can be obtained from the amplitude and the initial slope. Initial slope =  $\dot{p}(0)$

$$\begin{aligned} &= -(\omega P / 4 \pi K T) \kappa a^{-2} \sum_{m=1}^{\infty} D_m \xi_m^2 \\ &= \frac{-(\omega P / 4 \pi K T) B(b)}{(a^2 / \kappa \xi_1^2) B / \sum_{m=1}^{\infty} (-D_m) (\xi_m / \xi_1)^2} \\ &= \frac{A}{\tau C(b)} \end{aligned}$$

where  $\tau$  is the principal time constant

$a^2 / (2.4048)^2 \kappa$ , and  $C(b)$  is a correction factor to give the apparent time constant. The correction factor

$$C(b) = -B(b) / \sum_{m=1}^{\infty} D_m (\xi_m / \xi_1)^2,$$

is given in Table A-3 for various values of  $b$ .

TABLE A-3

b	$\approx 0$	0.20	0.25	0.30
C	1.48	1.44	1.35	1.32

## CONCLUSIONS

The absorptivity is given by

$$\alpha = 4\pi KTA/WPB, \quad (A-2)$$

where

K = gas thermal conductivity

T = ambient gas temperature

A = final amplitude of step response

W = beam power

P = nominal gas pressure

B = a function of b, the ratio of beam radius to cell radius,  
given in Table A-1.

The thermal diffusivity is given by

$$\kappa = \dot{p}(0) a^2 C / (2.4048)^2 A, \quad (A-3)$$

where

$\dot{p}(0)$  = the initial rate of pressure rise,

a = cell radius

C = a function of b given in Table A-3.

REFERENCES

- <sup>1</sup>Absorption of Light in Gases, First Annual Technical Summary Report Through 31 January 1966, Perkin-Elmer Corporation (Report No. 8361).
- <sup>2</sup>John William Strutt, Lord Rayleigh, "On Convection Currents in a Horizontal Layer of Fluid, When the Higher Temperature is on the Under Side", Scientific Papers, 6 (Cambridge, 1920) p.441, Eq. 46.
- <sup>3</sup>E.F. Barker and Arthur Adel, "Resolution of the Two Difference Bands of CO<sub>2</sub> Near 10μ". Physical Review, 44, (August 1, 1933) pp. 185-187.

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<p>Preliminary absorptivity data were taken with the spectrophone method and a 1.75 watt CO<sub>2</sub> laser. Test gases included pure CO<sub>2</sub>; a mixture of CO<sub>2</sub>, N<sub>2</sub> and He; and a sample of contaminated He. The measured absorptivity of CO<sub>2</sub> at 10.6 microns was <math>6.8 \times 10^{-4} \text{cm}^{-1}</math>. This value agrees closely with the absorptivity measured by conventional spectroscopy methods. The absorptivity of the contaminated He was on the order of <math>5.4 \times 10^{-5} \text{cm}^{-1}</math>.</p> <p>In the spectrophone method, a laser illuminates a closed sample chamber with end windows appropriate to the type of source laser. Any energy absorbed by the gas causes a temperature and pressure rise in the cell. Pressure rises as small as <math>0.02 \text{ dyne cm}^{-2}</math> may be observed with a pressure-measuring instrument such as a sealed capacitor microphone. In the experiment described above, the sample tube was 10 cm long. The absorption pressure signal from pure CO<sub>2</sub> was <math>630 \text{ dynes cm}^{-2}</math>. However, there is a spurious long-term pressure rise of about <math>1 \text{ dyne cm}^{-2} \text{sec}^{-1}</math>.</p> <p style="text-align: right;">(continued)</p>		



### 13. ABSTRACT (Continued)

These results indicate that absorptivities as weak as  $10^{-8} \text{ cm}^{-1}$  should be measurable when the spurious pressure rise is eliminated.

The spectrophone method with a ruby laser was used to obtain a spectrum of the water vapor absorption line at  $6943.8 \text{ \AA}$ . The sample was air at one atmosphere saturated with water vapor at room temperature. The peak absorptivity recorded was  $3 \times 10^{-6} \text{ cm}^{-1}$ . The linewidth was less than  $0.2 \text{ \AA}$ .

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